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LLNL-JRNL-600353

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November 9, 2012

Journal of Physics: Condensed Matter

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Pulsed-beam measurement of defect diffusion lengths in ion-bombarded solids

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(Dated: June 14, 2012)

Radiation-generated point defects in solids often experience dynamic annealing (DA) — diffusion and interaction processes after the thermalization of collision cascades. The length-scale of DA can be described by the characteristic defect diffusion length (L_d). Here, we propose to measure the L_d by a pulsed-beam method. Our approach is based on the observation of enhanced defect production when, for individual ion pulses, the average separation between adjacent damage regions is smaller than the L_d. We obtain a L_d of ~ 35 nm for float-zone Si crystals bombarded at room temperature with 500 keV Ar ions. This method is suitable for systematic studies of length scales of defect interaction processes in Si and other technologically relevant materials.

Despite many decades of extensive research, understanding response of solids to irradiation with energetic particles remains a major materials physics challenge.[1] This is directly related to the mesoscale nature and complexity of radiation damage phenomena. Collisional processes by which the incident particle slows down result in the formation of vacancies and interstitials and the development of collision cascades. This ballistic stage of defect production is considered to be well understood (excluding cases when cascades are non-linear).[1] After cascade thermalization, point defects can experience migration and interaction, commonly referred to as dynamic annealing (DA) processes. It is the DA that, in most practical cases, largely determines the form and extent of stable lattice damage in solids after irradiation and materials' "radiation-resistance."[1] Such DA processes are complex and remain poorly understood. They depend non-trivially on both the material itself and irradiation conditions that include energy, mass, dose, and dose rate of bombarding particles as well as target temperature.[1]

The length- and time-scales of DA can be described by characteristic diffusion lengths (L_d) and lifetimes (τ) of point defects. The L_d, which is the focus of the present study, describes the average distance over which defects diffuse outward from the ballistic cascade before they annihilate or get trapped at other lattice defects during the time τ after cascade thermalization. However, these basic parameters, L_d and τ, are still not well known even for arguably the best studied material system like single-crystalline Si. Indeed, for Si at room temperature (RT), a wide range of L_d values has been reported, from ~ 10 to 2000 nm.[2–12]

This situation is related to difficulties with direct measurements of the L_d and, possibly, to its expected dependence on irradiation conditions and the quality of the starting material. Many DA studies have traditionally involved measurements of the dependence of damage production on the dose rate when all the other experimental parameters are kept constant.[1–3,6,13,14] A dose rate effect is observed when τ is comparable to the average time interval between the formation of damage zones, originating from different collision cascades, at distances $\lesssim L_\mathrm{d}$. Hence, the difficulty of the dose rate effect approach is related to the fact that the spatial (L_d) and temporal (τ) contributions are convoluted, and their separation requires making assumptions about explicit defect interaction processes.[2,3,15]

The L_d can also be estimated from measurements of dopant diffusion profiles.[4,16–18] This, however, requires making additional assumptions about diffusion mechanisms and has further complications that such diffusion experiments are done at elevated temperatures (for example, $\gtrsim 600$ °C for Si), and, hence, their results have to be extrapolated to lower irradiation temperatures that are often of practical interest.

Other approaches to estimating L_d's include transmission electron microscopy[11,12] and studies of Si bombarded to ultra-low doses,[5–10] when the concentration of ballistically generated displacements is smaller than the concentration of free charge carriers. This latter method is based on a comparison of depth profiles of displacements predicted by ballistic calculations and measured by deep level transient spectroscopy (DLTS), spreading resistance profiling (SRP), or photoluminescence (PL). However, this approach, although important for understanding defect trapping centers in as-grown Si, is challenging to apply to many cases of practical importance, such as ion implantation doping and nuclear material performance, which involve orders of magnitude larger doses and/or material systems that are unsuitable for DLTS, SRP, or PL characterization. This method is also complicated by a contribution from ion channeling, leading to the appearance of exponentially decaying tails in defect distributions, qualitatively similar to those expected for a process of trap-limited diffusion.[9]

In contrast to traditional dose-rate effect studies, a pulsed ion beam method can be used to separate spatial and temporal information. We have recently demonstrated[19] that the DA time constant τ can be measured directly by studying the dependence of lattice disorder on the time interval of the *passive* part of the beam cycle, t_off. The inset in Fig. 1 shows a time dependence of the dose rate in such pulsed ion beam experiments and defines the pulsing related parameters: t_on, t_off, and F_on.

With this method, a τ of ~ 5 ms has been measured for Si irradiated at RT with 500 keV Ar ions, significantly clarifying previous estimates of τ in RT Si, ranging over 12 orders of magnitude.[19]

In this letter, we demonstrate how the pulsed beam approach can also be used for a direct measurement of the $L_{\rm d}$ by studying the dependence of lattice disorder on the duration of the *active* part of the beam cycle, $t_{\rm on}$. With this method, we obtain a L_d of $\sim$ 35 nm for Si crystals bombarded at RT with 500 keV Ar ions.

Float-zone grown (100) Si single crystals with a resistivity of $\sim 5\ \Omega$ cm were bombarded at RT with 500 keV $^{40}Ar^{+}$ ions at 7° off the [100] direction. The 4 MV ion accelerator (National Electrostatics Corporation, model 4UH) at Lawrence Livermore National Laboratory was used for both ion irradiation and ion beam analysis. As described in detail previously,[19] in order to avoid complexity related to differences between instantaneous and average dose rates inherent to experiments with rastered ion beams, all irradiations were performed in a broad beam mode. Beam pulsing was achieved by applying high voltage pulses to a pair of plates deflecting the beam off the final beam defining aperture.[19] The total dose was split into a number of equal pulses with a dose per pulse of $t_{\rm on}F_{\rm on}$ (see the inset in Fig. 1). Each sample was irradiated to a total dose of 2×10^{14} cm^{-2} with a constant $F_{\rm on}$ of $\sim 1.6\times10^{13}$ cm^{-2} s^{-1}. Such irradiation produces sub-amorphization damage in a non-linear region of the damage buildup curve,[19] where DA processes are particularly pronounced.[13] The duration of the passive part of the cycle ($t_{\rm off}$) was kept constant at 100 ms, and the dependence of lattice damage on $t_{\rm on}$ (varied from 0.5 to 100 ms) was studied.

The lattice disorder was measured *ex-situ* by Rutherford backscattering/channeling (RBS/C) spectrometry with 2 MeV $^{4}He^{+}$ ions incident along the [100] direction and backscattered into a detector at 164° relative to the incident beam direction. All RBS/C spectra were analyzed with one of the conventional algorithms[20] for extracting the effective number of scattering centers (referred to below as "relative disorder").

Figure 1 shows selected depth profiles of lattice disorder in Si bombarded with all the parameters, except for $t_{\rm on}$, kept constant. The duration of the passive part of the cycle, $t_{\rm off} = 100$ ms, was chosen much larger than the defect stabilization time τ, which is ~ 5 ms for these conditions.[19] Profiles in Fig. 1 reveal two distinct peaks. One peak is positioned at or near the surface. The other, main peak is centered on $\sim$ 450 nm, which corresponds to the position of the maximum nuclear energy loss of 500 keV Ar ions ($\sim$ 445 nm from TRIM code calculations).[21] Such a bimodal damage accumulation behavior is consistent with a number of previous reports.[2,3,13,14,19] It points to an important role of the sample surface in DA (more accurately, the interface between the Si crystal and its native oxide layer). Figure 1 also reveals that the amount of stable disorder in the bulk peak increases with increasing $t_{\rm on}$, while the damage

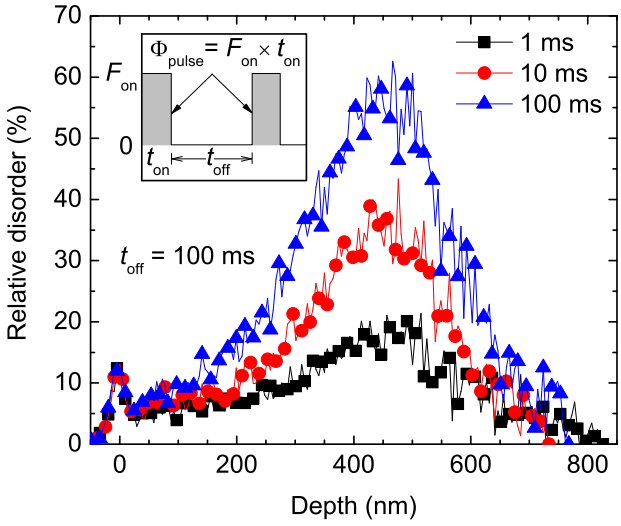

FIG. 1. (Color online) Selected depth profiles of relative disorder in Si bombarded at RT by 500 keV Ar ions with a pulsed beam with different values of $t_{\rm on}$ (given in the legend in units of 10^{-3} s) and all the other parameters fixed (total dose = 2×10^{14} cm^{-2}, $t_{\rm off} = 100$ ms, and $F_{\rm on} \approx 1.6\times10^{13}$ cm^{-2} s^{-1}). The inset shows a schematic of the time dependence of the dose rate, defining $t_{\rm on}$, $t_{\rm off}$, $F_{\rm on}$ (the maximum instantaneous dose rate), and Φ_{pulse} (the dose per pulse).

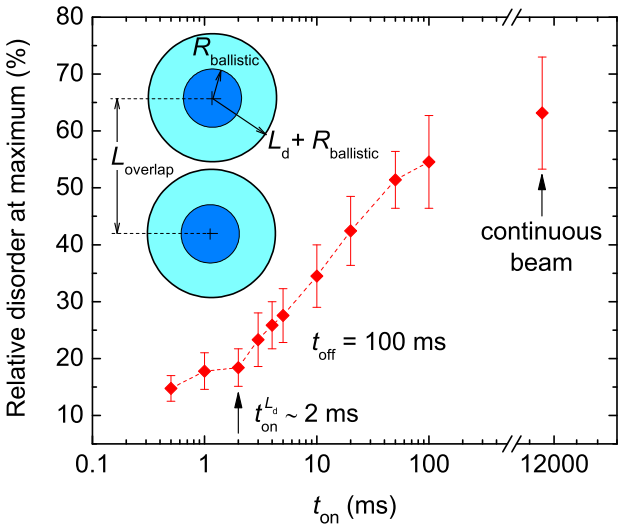

FIG. 2. (Color online) Dependence of relative disorder at the maximum of the bulk defect peak in Si bombarded at RT by a pulsed beam of 500 keV Ar ions on the duration of the active part of the cycle, $t_{\rm on}$, and all the other parameters fixed as in Fig. 1. The maximum damage level produced by a continuous beam ($t_{\rm off} = 0$) is also shown. A critical value of $t_{\rm on}$ above which the damage level is rapidly increases is labeled as $t_{\rm on}^{L_{\rm d}}$ and marked by an arrow. The inset shows a schematic of cascades in a slice made perpendicular to the beam direction, defining parameters $R_{\rm ballistic}$ (average radius of ballistic cascades), $L_{\rm d}$ (characteristic defect diffusion length), and $L_{\rm overlap}$ (average lateral distance between the centers of collision cascades in one pulse).

accumulation within ~ 40 nm from the sample surface is essentially independent of t_{on}. This observation suggests a difference in mechanisms of DA processes in the crystal bulk and at the surface. It is also consistent with several previous reports.[2,13,14,19]

The dependence of the level of maximum bulk disorder on t_{on} is better illustrated in Fig. 2, wiht error bars corresponding to peak-to-peak noise in RBS/C-derived disorder profiles such as shown in Fig. 1. Figure 2 clearly shows a trend of increased disorder with increasing t_{on} above a certain critical value of ~ 2 ms, which we will refer to as $t_{on}^{L_d}$. For $t_{on} \lesssim t_{on}^{L_d}$, the disorder level is essentially independent of t_{on}. Such a $t_{on}^{L_d}$ is related to the defect diffusion length, L_d. Indeed, t_{on} determines the dose delivered in every pulse, $t_{on}F_{on}$ (see the inset in Fig. 1). Such a dose per pulse in turn determines the average lateral distance between individual collision cascades for each pulse: $L_{overlap} \approx 1/\sqrt{t_{on} \cdot F_{on}}$. For pulses with small t_{on}, $L_{overlap}$ is larger than the average lateral size of damage zones associated with individual collision cascades. As illustrated in the inset of Fig. 2, such damage zone sizes are defined by both the size of ballistic cascades ($R_{ballistic}$) and the L_d. For cases of low t_{on} and $L_{overlap} > 2(L_d + R_{ballistic})$, mobile defects produced in different cascades cannot interact since $t_{off} \gg \tau$. Hence, DA processes involving mobile defects generated in different ion pulses are negligible. In this case, the buildup of stable damage is independent of the pulse duration (t_{on}), as observed in the experiment (Fig. 2).

For $t_{on} \gtrsim t_{on}^{L_d} = 1/(4F_{on}(L_d + R_{ballistic})^2)$, however, defects produced in different cascades begin to interact. This results in increased stable disorder due to nonlinear defect interaction processes. Various possible defect interaction scenarios could lead to such non-linearity. For example, during the active part of each cycle, the efficiency of stable defect production is different before and during the regime when a stationary population of mobile (unstable) defects is reached. The quantitative dependence of the buildup of stable disorder on t_{on} is determined by specific defect interaction processes, which are still poorly understood and debatable even for Si at RT.[2–12,14,15] We, however, emphasize that the determination of the L_d based on the threshold value of t_{on} proposed here does not require the knowledge of these specific defect interaction processes since it is not based on an analysis of the non-linearity of the damage buildup behavior.

From Fig. 2, a $t_{on}^{L_d}$ of ~ 2 ms corresponds to a L_d of ~ 35 nm, given that $R_{ballistic}$ is only $\sim 1-2$ nm.[21,22] This is comparable with several previous estimates of a L_d of $\sim 10-50$ nm with other methods for different types of Si irradiated at RT with ions or electrons.[2,3,5,8,10–12] Interestingly, a L_d of ~ 35 nm is also consistent with a distance of ~ 40 nm from the sample surface where damage is essentially independent of t_{on} (see Fig. 1 and a discussion above), suggesting that the sample surface acts as an efficient sink for mobile defects. A L_d of ~ 35 nm is, however, much smaller than a L_d of $\sim 300-2000$ nm estimated in Refs. 5, 7, and 10 based on DLTS, SRP, or PL measurements. This discrepancy could be attributed to channeling effects discussed by Nielsen et al.[9] or to a possible dependence of the L_d on irradiation conditions. Future systematic studies should clarify it.

Our results can also be used to estimate the diffusion coefficient of the defects dominating DA processes. With $\tau = 5$ ms (Ref. 19) and $L_d = 35$ nm, $D = L_d^2/\tau \approx 2 \times 10^{-9}$ cm^2 s^{-1}. Inerestingly, this value is close to the value of the RT diffusion coefficient of vacancies in Si ($\sim 4 \times 10^{-9}$ cm^2 s^{-1}).[23] More work is, however, currently needed to ascertain if the primary mobile defect species determining the RT DA processes in ion-bombarded Si are isolated vacancies[2,3,10,13] rather than other possible defects such as interstitials,[6–8] di-interstitials,[24] "bond defects,"[25] or some combination of several interacting defect species.

Finally, the method to measure the L_d proposed here could also be applied to test the models of damage buildup in solids, to study the dependence of the L_d on irradiation conditions, and to measure the L_d in other technologically relevant materials. Of particular interest is the knowledge of length scales of DA processes when designing materials with improved "radiation-resistance" via controlled interaction of mobile defects with surfaces and interfaces.[26] In this case, the diffusion length determines the required dimensions of "radiation-resistant" nanostructures.

In conclusion, we have demonstrated an experimental method to measure the effective defect diffusion length (L_d) after cascade thermalization. Our approach can be summarized as follows: (i) the total dose is chosen in the nonlinear regime of the damage buildup behavior, and $t_{off} >> \tau$ is selected; (ii) samples are bombarded with a pulsed ion beam, and the dependence of the level of stable lattice disorder on t_{on} is measured (with all the other irradiation parameters kept constant); and (iii) the L_d is calculated based on the threshold value of $t_{on}^{L_d}$ (above which the damage level exhibits a dependence on t_{on}) as $L_d \approx 1/2\sqrt{t_{on}^{L_d} \cdot F_{on}} - R_{ballistic}$, where the average lateral size of ballistic cascades ($R_{ballistic}$) can be estimated from ballistic calculations such as the TRIM code.[21,22] With this method, we have measured a L_d of ~ 35 nm in Si irradiated at RT with 500 keV Ar ions. These results should stimulate future studies of length scales of defect interaction processes in Si and other technologically relevant materials.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344. L.S. thanks the support from NSF grant No. 0846835, and M.T.M. acknowledges the LLNL Lawrence Scholar Program for funding.

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